

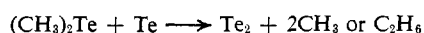
ference from the cracking pattern of the parent DMT. In 50 msec little decay had taken place.

The addition of ground-state tellurium atoms to olefins to form short-lived adducts resembles the behavior of selenium atoms which also form short-lived adducts with olefins.<sup>4-7</sup>

Some quantitative rate measurements were also carried out. Relative concentrations of  $\text{Te}(^3\text{P}_2)$  atoms were estimated by photometry of the 2143- and 2259-Å absorption lines. A Beer-Lambert factor of  $0.5 \pm 0.1$  has been established for the atomic transitions, relating changes in optical density to atomic concentrations.

Atomic decay has been investigated with various chaperons in the pressure range 30–300 Torr. Hydrogen,  $\text{CH}_4$ , and *i*- $\text{C}_4\text{H}_{10}$  were found to be efficient in bringing about spin-orbit relaxation of excited atoms,<sup>12</sup> while  $\text{O}_2$ ,  $\text{CO}_2$ , and Ar were much less efficient. The excitation energies of the  $^3\text{P}_0$  and  $^3\text{P}_1$  states of Te are 4707 and 4751  $\text{cm}^{-1}$ , respectively, and since  $\omega_e$  for  $\text{H}_2$  is 4395  $\text{cm}^{-1}$ , the high relaxation efficiency of  $\text{H}_2$  may be attributed to a resonance effect.

The decay of ground-state atoms has been found to be first order in all cases studied and the rate (in the absence of olefins) to be dependent on the concentration of DMT. Plate photometry showed the concentration of DMT to be constant throughout the atomic decay and was used to estimate the absolute concentration. A plot of the first-order rate constant in a variety of inert gases against DMT pressure during the decay was found to be a straight line passing through the origin. The second-order rate constant obtained was  $1.7 \times 10^{11}$  l. mole<sup>-1</sup> sec<sup>-1</sup>. This corresponds to a reaction between tellurium atoms and DMT at virtually every collision. The reaction implied would appear to be



or the formation of an intermediate adduct which may then decompose to these products.

The presence of an olefin accelerates the atomic decay. From the observed rate increase it was possible to derive rate constants for the addition reactions, olefin

(12)  $\text{Te}(^3\text{P})$  atoms would not be expected to attack paraffins or hydrogen, and no evidence has been found for such reactions.

+ Te  $\rightarrow$  epitelluride, for ethylene and propylene. These, along with the corresponding values for other members of the group, are shown in Table I. All rate

**Table I**

	O( <sup>3</sup> P)	S( <sup>3</sup> P)	Se( <sup>3</sup> P)	Te( <sup>3</sup> P)
$k_{\text{C}_2\text{H}_4}$	$3 \times 10^{10a}$ $6 \times 10^{10b}$	$7 \times 10^{10c}$	$1 \times 10^{10e}$	$2 \times 10^7$
$k_{\text{C}_2\text{H}_6}/k_{\text{C}_2\text{H}_4}$	5.8 <sup>a</sup>	6.8 <sup>d</sup>	3.5 <sup>e</sup>	10

<sup>a</sup> Reference 2. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> Reference 3. <sup>e</sup> References 4–7.

constants are in units of l. mole<sup>-1</sup> sec<sup>-1</sup>. From the data, the Te atom addition is somewhat slower than the addition of O, S, or Se atoms and it is also more selective.

As an alternative source of tellurium atoms the flash photolysis of  $\text{H}_2\text{Te}$  has been briefly examined. Ground-state and spin-orbit excited Te atoms were observed along with  $\text{Te}_2$ . The 2750–2850-Å band progression was absent. A new transient species absorbing at about 2155 Å has been detected. The spectrum shows considerable rotational fine structure and may be due to the  $\text{TeH}$  radical.

Both first- and second-order plots of the atom decay showed curvature consistent with a transition from an initial second-order process for the removal of atoms to a first-order process.

A standard flash photolysis apparatus was employed. Spectra were recorded with a medium quartz spectrograph on Kodak 103a-O plates sensitized for the far-uv by sodium salicylate and developed for 4 min in Kodak D19 developer. Plates were photometered on a Joyce-Loebl Mark III recording microdensitometer.

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## Additions and Corrections

**Structure of Chlorophyll *c*** [*J. Am. Chem. Soc.*, **88**, 5037 (1966)]. **Structure of Phycocyanobilin** [*J. Am. Chem. Soc.*, **89**, 3642 (1967)]. **A Perturbation Molecular Orbital Approach to the Interpretation of Organic Mass Spectra. The Relationship between Mass Spectrometric, Thermolytic, and Photolytic Fragmentation Reactions** [*J. Am. Chem. Soc.*, **90**, 5780 (1968)]. **Application of the Perturbation Molecular Orbital Method to the Interpretation of Organic Mass Spectra. The Hexahelicene Rearrangement and Other Electrocyclic Mass Spectrometric Reactions** [*J. Am. Chem. Soc.*, **90**, 5788 (1968)]. **Negative Ion Mass Spectra of Benzene, Naphthalene, and Anthracene. A New Technique for**

**Obtaining Relatively Intense and Reproducible Negative Ion Mass Spectra** [*J. Am. Chem. Soc.*, **90**, 6570 (1968)]. By R. C. DOUGHERTY, *et al.*, Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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**Synthesis of Sugar-like Phosphates by the Oxyphosphorane Condensation. Reaction of Glyoxal with Trialkyl Phosphites and Preparation of Phosphate Esters**